

# PATENT SPECIFICATION

NO DRAWINGS

1.118,741

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Date of Application and filing Complete Specification: 25 May, 1965.

No. 22025/65.

Application made in United States of America (No. 372,113) on 2 June, 1964.

Application made in United States of America (No. 451,033) on 26 April, 1965.

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Index at acceptance:—D1 P(A1, A17, A23, AX, B2A1, B2A2, B2B1, B5A, B5B, B5C, B5X, C1J, C2A4, C2A12A9, C2A12B1, C2A12B2, C2A12B5, C2B3, C2C1, C2C2, C2C3, C2C5, C2C9, C2C17, C2CX); A5 E2; C3 U(2AX, 4J); D2 B(14A, 14F, 14X)

Int. Cl.:—D 06 m 13/12

## COMPLETE SPECIFICATION

### Aldehyde Fixation of Cellulosic Material or Starch

## ERRATA

SPECIFICATION No. 1,118,741

Page 1, line 54, after "carbamate" delete "and"

Page 2, line 1, for "gloxal" read "glyoxal"

Page 2, line 21, for "hydroxadipaldehyde" read "hydroxyadipaldehyde"

Page 3, line 21, for "formaldehyle" read "formaldehyde"

Page 4, line 69, for "and" read "wet"

Page 5, Table 1, last column, Heading, for "Pill-In" read "Pull-In"

Page 6, Table 4, footnote, third line, for "ATACC" read "AATCC"

Page 8, line 18, after "and" insert "is"

Page 11, under Gauge (Dry), sixteenth line, for "20" read "30"

Page 12, line 29, for "comprehensive" read "compressive"

Page 12, line 40, for "coloured" read "colored"

Page 12, lines 73 and 74, after "laundering" delete "This example throughout multiple laundering"

Page 12, line 77, after "press" delete "20"

Page 14, lines 40 and 44, after "and" insert "as"

Page 14, lines 63, 64 and 66, after "unsubstituted" insert "hyphen"

The words "fibre" and "fibres" spelt inconsistently throughout.

THE PATENT OFFICE

5th August 1968

[Price 4s. 6d.]



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## COMPLETE SPECIFICATION

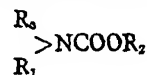
## Aldehyde Fixation of Cellulosic Material or Starch

We, WEST POINT-PEPPERELL, INC., a Corporation of the State of Georgia, of West Point (no Street address), Georgia, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

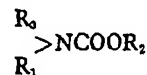
This invention relates to a novel and improved process for the fixation of an aldehyde on cellulose, cellulose esters and starch. It is known to fix aldehydes such as formaldehyde for example, on cellulose, cellulose esters and starch. In such prior art processes, however, it has been found difficult to predetermine the amount of formaldehyde fixed, and to reproducibly control the amount of formaldehyde fixed. Also, in some instances, there is required the use of concentrated solutions of formaldehyde with high amounts of acid that tend to degrade the material being treated. Additionally, in such prior art processes, the efficiency is low in the sense that only a small amount of the formaldehyde used is actually bound on the substrate, such as cellulose, the remainder being lost.

It has previously been proposed to apply a precondensate of formaldehyde with an alkyl carbamate, e.g. formaldehyde-methyl carbamate precondensate, to cellulose. In such procedure, there is a fixation of the nitrogen of the precondensate to the cellulose molecule, as can be verified by the significant increase in nitrogen content of the treated cellulose over the relatively minor amount of nitrogen present in the untreated cellulose material.

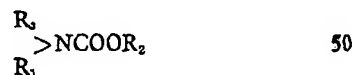
According to the present invention a process of fixing an aldehyde on cellulose, a cellulose ester or starch is provided which comprises the steps of treating the material with an aqueous composition containing (1) an aldehyde and a carbamate having the formula



(2) an aldehyde-carbamate condensation product wherein the carbamate has the formula



or (3) an aldehyde together with an aldehyde-carbamate condensation product wherein the carbamate has the formula



wherein  $R_1$  and  $R_2$  are each hydrogen or alkyl or carbocyclic aryl radicals at least one of  $R_1$  and  $R_2$  representing a hydrogen atom in the case of an aldehyde-carbamate and condensation product, and  $R_2$  is an unsubstituted alkyl or a cycloalkyl or carbocyclic aryl radical, and heating the treated material at a temperature sufficient to fix the aldehyde on the material but insufficient to cause any substantial nitrogen fixation.

Aqueous mixtures of formaldehyde and alkyl carbamates wherein the mole ratio of formaldehyde to carbamate is at least 3:1 are described and claimed in our copending Application No. 7051/68, Serial No. 1,118,742.

The cellulose can be in the form of cotton, alpha cellulose, regenerated cellulose or rayon, e.g. cuprammonium rayon or viscose rayon, or paper. As cellulose esters, there can be employed esters containing reactive hydroxyl groups, for example, cellulose acetate, cellulose acetate-butyrate or cellulose acetate-propionate. As the aldehyde, there can be em-

SEE ERRATA SLIP ATTACHED

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ployed formaldehyde, gloxal, pyruvic aldehyde, glutaraldehyde, acetaldehyde, propionaldehyde, butyraldehyde or hydroxyadipaldehyde. The preferred aldehyde is formaldehyde.

- 5 The cellulose material can be blended with synthetic fibres such as polyesters, e.g. polyethylene terephthalate, acrylic fibres, e.g. polyacrylonitrile, acrylonitrile-vinyl chloride copolymer fibres (85:15 or 15:85), nylon, e.g. polymeric hexamethylene adipamide, polypropylene, propylene ethylene copolymers, spandex or vinyl-chloride vinyl acetate copolymer fibres, e.g. (87:13). The fibres may comprise a substrated percentage of regenerated cellulose fibres, especially at least 35% by weight of viscose rayon fibre.

- For special purposes where extra rigidity is required, it is desirable to employ glyoxal. When less rigidity than that imparted by formaldehyde is desired, other aldehydes such as acetaldehyde or hydroxyadipaldehyde can be used. Of course, mixtures of aldehydes can be employed.

- The carbamate may be one wherein  $R_1$  and  $R_2$  in the formula above each represent hydrogen and  $R_2$  represents alkyl or cycloalkyl. Thus, there can be employed for example, methyl carbamate, ethyl carbamate, propyl carbamate, isopropyl carbamate, butyl carbamate, amyl carbamate, hexyl carbamate, octyl carbamate, decyl carbamate, dodecyl carbamate, cyclohexyl carbamate or octadecyl carbamate. Mixtures of carbamates can be employed, e.g. the eutectic mixture of 52% by weight of ethyl carbamate and 48% by weight of methyl carbamate.

- The carbamate may also be an aryl carbamate, and there can be employed for example, phenyl carbamate, *o*-tolyl carbamate, *p*-tolyl carbamate, *m*-tolyl carbamate, *p*-butylphenyl carbamate,  $\alpha$ -naphthyl carbamate,  $\beta$ -naphthyl carbamate, or 2,4-xylyl carbamate.

- The carbamate may also be an N-hydrocarbyl substituted carbamate and there can be used for example N-phenyl isopropyl carbamate, N-phenyl phenyl carbamate, N-*p*-tolyl ethyl carbamate, N-phenyl methyl carbamate, N-phenyl ethyl carbamate, N-methyl phenyl carbamate, N-ethyl phenyl carbamate, N-methyl methyl carbamate, N-methyl ethyl carbamate, N-methyl decyl carbamate, N-ethyl methyl carbamate, N-ethyl ethyl carbamate, N-dodecyl methyl carbamate, N-butyl cyclohexyl carbamate, N,N-diethyl ethyl carbamate, N,N-dimethyl ethyl carbamate, N,N-diethyl methyl carbamate or N,N-diphenyl methyl carbamate.

- Higher temperatures are generally required to activate the aryl carbamates and the N-hydrocarbyl carbamates than is the case with the lower alkyl carbamates such as methyl carbamate and ethyl carbamate. Hence, these latter compounds are usually preferred.

- Preferably, however, there is employed a mixture of the aldehyde and alkyl carbamate,

since it has been found that the reaction proceeds more smoothly, and shorter process times are normally required. Additionally, the use of the mixture eliminates the expense of preforming the aldehyde-alkyl carbamate condensation product.

When utilizing an aldehyde-alkyl carbamate condensation product, it is important that the heating of the treated product be at a temperature not above 300°F, because if a higher temperature, such as 350°F, is utilized, instead of the condensation product decomposing to form ammonia, carbon dioxide and an alcohol, the competing reaction of nitrogen fixation to cellulose through the methylol group tends to take place in accordance with prior art procedures.

On the other hand, when utilizing an aqueous mixture of an aldehyde and a carbamate, the temperature of heating the product in order to fix the formaldehyde to cellulose, cellulose esters or starch can be varied much more widely. Thus, not only can temperatures of 180°F. to 300°F. be employed, but there can be utilized more elevated temperatures, such as 350°F. or 400°F.

Unless otherwise specified, throughout the specification and claims, the temperature of heating the product connotes the actual temperature to which the product is elevated, as determined for example by surface pyrometry or infrared pyrometry in the case of moving fabrics; as will be understood, this will normally correspond to a somewhat higher oven temperature, or the desired temperature level may be achieved by radiation from heat sources themselves at a considerably higher temperature. The apparent reason for this is that the reaction to form the methylol carbamate proceeds relatively slowly, whereas the reaction to fix the formaldehyde to cellulose or the like goes quite rapidly. Product temperatures of 180—300°F. are preferred, as less likely to degrade the product. A preferred cure or fixation temperature range for cotton is 200—220°F.

Surprisingly, it has been found that the carbamate acts only as a carrier in assisting the formaldehyde to become fixed on the cellulose, cellulose esters or starch, but does not itself become fixed in any significant amount to the cellulose material being treated.

It has been observed that in order to aid in fixing formaldehyde or other aldehyde on cellulose, cellulose esters or starch, there should be employed at least 0.1%, and more preferably at least 0.3% by weight of methyl carbamate, for example, in the aqueous solution or dispersion, or equivalent molar percentage by weight of other carbamate used. It is difficult to maintain control of the amount of formaldehyde fixed to the cellulose if less than 0.1% of methyl carbamate or equivalent is in the solution or dispersion. For more control of the reproducibility of

formaldehyde fixation, it is desirable to use at least 0.5% of methyl carbamate or equivalent in the aqueous system. Throughout the present specification and claims, unless otherwise indicated, all parts and percentages are by weight.

Higher amounts of carbamate, e.g., 1% to 5% or more by weight of methyl carbamate (or other carbamate) in water, can be employed, but normally there is no advantage in utilizing excess amounts since they do not appear to give better results than does 1% or so, which would justify the increased cost of the reagent. Preferably, the alkyl carbamate employed is a lower alkyl carbamate; most preferably methyl carbamate, ethyl carbamate or mixtures thereof.

The aldehyde is employed in the aqueous system in an amount normally between 1% and 8% thereof, although if relatively larger amounts of formaldehyde are to be fixed on to the cellulose or other material, there can be used as much as 10% or 15% or more of aldehyde. Desirably, the aldehyde is employed in an amount of at least 3 moles per mole of carbamate, and can be employed in an amount as much as 60 moles or even 100 moles per mole of carbamate. Generally, lower mole proportions of aldehyde are preferred, and one of the advantages of the present invention is that lower amounts of aldehyde are required in the aqueous treating system, for the amount of formaldehyde fixed on the cellulosic material, than is the case with prior art processes. Additionally, the problem of formaldehyde odour is thereby materially reduced.

When treating cotton, alpha cellulose, starch or paper, there is usually employed an aqueous solution containing 1.25—4.0% of formaldehyde, in order to fix 0.25—1.25% formaldehyde, on to the treated material.

When treating rayon or cellulose esters, there is usually employed an aqueous solution containing 2.5—8.0% of formaldehyde, in order to fix 0.50—2.5% formaldehyde, on to the treated material. Of course, with any of the materials there can be employed a solution containing 1.25—8.0% of formaldehyde, to fix 0.25—2.5% formaldehyde, by weight of the treated material.

When employing a carbamate-aldehyde condensation product, there is preferably added to the solution enough aldehyde to bring the aldehyde level to at least 3 moles of aldehyde (including that in the condensation product) per mole of carbamate present in the condensate.

The mixture of aldehyde and alkyl carbamate, e.g. formaldehyde and methyl carbamate, can be shipped as an aqueous mixture containing the two materials in any of the proportions indicated above. This aqueous mixture can be relatively concentrated at the time of shipment and can then be diluted with water to obtain the desired amount of ingredi-

ents for the bath through which is passed the cotton, for example. For stability purposes, the mixture which is shipped is preferably neutral, although it can be alkaline or acidic.

The bath through which the cotton or other material is passed is generally acidic or has a latent acid catalyst therein. Suitable acids and latent acid catalysts are, for example, formic acid, hydrochloric acid, ammonium chloride, magnesium chloride, calcium chloride, zinc nitrate, zinc chloride, zinc fluoroborate, or mixtures thereof. Since little catalyst is required, it may be supplied by residual acid-forming salt, such as ammonium chloride, on the goods being treated.

Fixation of an aldehyde on the material, utilizing the alkyl carbamate carrier has also been found to be operative on the alkaline side, e.g. using catalysts such as sodium carbonate, potassium carbonate, sodium bicarbonate, potassium bicarbonate, sodium hydroxide or potassium hydroxide. For most purposes, acid catalysts are preferred. As in the former case, the alkaline catalyst may be supplied on the goods being treated. When catalyst is added to the treating bath, it is normally used in an amount of 0.1—2% of the bath, although this can be varied.

The normal procedure for applying the aldehyde and carbamate mixture to the material is to pass a fabric, fibres, sheet or continuous yarn through the aqueous mixture of aldehyde and carbamate, and then to run the thus impregnated material through squeeze rolls to remove excess solution. In the case of yarn, the procedure may be to pass the solution through packages of the yarn in a kier. A similar process can be employed in treating starch.

The process of the present invention has the advantage over prior art processes of fixing aldehyde to material such as those described above, with good reproducibility of results, particularly when the alkyl carbamate is present in the treating mixture in an amount of at least 0.5%. A further advantage is that any desired amount of aldehyde can be fixed to the cellulose or the like, simply by controlling the amount of aldehyde in the aqueous mixture.

Of course, there can be added to the aqueous mixture of aldehyde and alkyl carbamate (or aldehyde-alkyl carbamate condensation product), conventional additives, such as wetting agents, hand modifiers, softeners, lubricants and brighteners.

While formaldehyde is preferably employed as such in the aqueous mixture, it is possible to utilize sources of formaldehyde such as paraformaldehyde, trioxane, and hexamethylenetetramine. In the case of such materials, however, there is a slight lengthening of the overall time of the process in order to permit the breakdown of these materials to

monomeric formaldehyde. For maximum efficiency, it has been found that a mole ratio of formaldehyde to alkyl carbamate of 12.5:1 gives best results. The present process is simpler to operate than the prior art procedures, and furthermore has the advantage that it is unnecessary to employ therein concentrated acid solutions which are not only difficult to work with, but furthermore degrade the material. Moreover the degree of aldehyde fixation is readily and precisely controllable and reproducible. The aldehyde is substantially permanently fixed, proof against repeated washing, by a process which is efficient, economical and rapid.

An outstanding advantage of the process resides in the circumstance that formaldehyde may be fixed on the base material, for example on cotton yarn or fabric, with considerable reduction in loss of strength as compared with conventional resin finishing processes while imparting wash-and-wear properties and crease-resistance.

In the conventional resin finishing processes loss of 40 to 50% of original strength is common, and may exceed 50%. This sizable loss in strength is commonly compensated for by providing extra strength (and material) in the greige goods, at added cost. In the present process, the loss of strength is commonly only 15—25% and rarely over 30%. It is believed that this favourable result is due primarily to three circumstances: the low temperature of drying that is required to fix the aldehyde, as compared to the high temperatures of normal resin curing conditions, the low concentration of catalyst used, and the fact that drying need not be carried to the end point of zero moisture content. Excellent results have been obtained with drying to a residual moisture content of 2—4% measured with a resistance type moisture measuring device. For very best re-

sults the fabric is carried to the point of substantially being bone dry.

The process of the present invention also imparts better whiteness retention to cellulose fabrics, e.g. viscose rayon fabrics, cotton fabrics and fabrics containing blends of synthetic and cellulosic fibres, and improved permanent crease retention properties.

The present invention is also important in greatly reducing the swelling properties of cellulosic fabrics especially non-woven viscose rayon fabrics.

This is particularly true in the case of viscose rayon, especially non-woven viscose rayon fabrics. Consequently the aldehyde and carbamate treatment of the present invention not only gives a cellulosic product, e.g. viscose rayon, of reduced swelling properties, but concomitant therewith yields improved stabilization against shrinkage.

The wash-wear fabrics of this invention do not retain chlorine or otherwise discolour or pick up soil in the course of repeated washing. Cellulosic fabrics treated according to the invention are mildew-proof and rot-resistant and paper treated according to the invention has improved and strength properties.

#### EXAMPLE I

Generally, the border yarns in towels shrink more than the rest of the towel. In order to overcome this defect, a series of towel border cotton yarns were treated in a kier with an aqueous mixture containing 1% methyl carbamate, 0.5% magnesium chloride hexahydrate, 0.5% formic acid, 1.2% sodium chloride, 0.17% of a dimethyl polysiloxane oil (softener), and the amounts of formaldehyde indicated below. After the treatment with the aqueous solution, the yarns were dried at 200°F. The treated yarns were then woven into the borders of cotton towels with the results indicated in the following table:

TABLE I

Sample	Molar Ratio Formaldehyde: Methyl Carbamate	% Formaldehyde		% Nitrogen		
		Yarn in Finished Towel	Yarn in Towel Laundered 30 Times	Yarn In Finished Towel	Yarn In Towel Laundered 30 Times	Border* Pull-In In 30 Launderers
1	2.5:1**	0.14	0.13	0.03	0.05	3.1%
2	5.0:1	0.28	0.30	0.05	0.05	-0.2
3	7.5:1	0.56	0.56	0.07	0.07	-0.8
4	10.0:1	0.77	0.72	0.08	0.04	-1.9
5	12.5:1	1.13	0.95	0.07	0.07	-1.2
6	2.5:1	0.16	0.16	0.04	0.03	1.6
7	Untreated Control	—	—	0.03	0.07	6.3
(Treated Yarn Average)				0.058	0.052	

$$\text{*Border Pull-in} = \frac{\text{Width of Towel Body} - \text{Width of Towel Border}}{\text{Width of Towel Body}} \times 100$$

(i.e., Differential Shrinkage)

\*\*A precondensate of methyl carbamate and formaldehyde was employed.

5 If the methyl carbamate had been affixed to the yarn, the amount of nitrogen would have been at least 0.26% for the sample having 1.13% of formaldehyde in the yarn (Sample 5).

The strength retention of the yarns treated in this example was very good. It is significant that strength retention was not dependent upon the level of formaldehyde fixed in the yarn. The strength retention is indicated in the following table.

10

TABLE 2

Sample	Skein Breaking Strength	% Retention	Single End Break	% Retention
1	314 lb.	76	5.20 lb.	69
2	298	72	5.32	71
3	306	74	5.33	71
4	316	77	5.37	72
5	316	77	5.63	75
6	263	64	5.07	68
7—Control	411	—	7.48	—

5 The strength retentions appearing above were based on bleached, mercerized yarn taken immediately before treatment with methyl carbamate and formaldehyde. When the strength retention calculation is based on the greige, mercerized yarn (6.37 lb. single end break), the state at which yarn strength is normally determined, strength retention of the above yarns is from 80 to 88 per cent.

## EXAMPLE II

10 Cotton yarn in a kier was saturated with an aqueous mixture containing 0.5% magnesium chloride hexahydrate, 0.5% formic acid, 0.3% methyl carbamate and the indicated amounts of formaldehyde. The yarns were then vacuum extracted and dried at 180°F to 2—3% residual moisture.

TABLE 3

Sample	% Formaldehyde in Mix	% Formaldehyde on Scoured Yarn	Molar Ratio Formaldehyde to Methyl Carbamate
1	1.5	0.37	12.5:1
2	1.5	0.40	12.5:1
3	2.5	0.52	20.8:1
4	2.7	0.52	22.5:1

20 The amount of fixed formaldehyde on the yarn is usually about 20 to 25% of the formaldehyde content of the aqueous mixture.

## EXAMPLE III

An aqueous mixture containing 5% for-

maldehyde, 1% methyl carbamate and 1% magnesium chloride hexahydrate was padded on a bleached enameling cotton duck at 55—60% wet pickup. The fabric was barely dried at 180°F (about 10% moisture), and heated at the indicated temperatures and times.

TABLE 4

Temperature °F.	Time Minutes	% Formaldehyde <sup>(2)</sup> Fixed on Fabric	% Nitrogen on Fabric	Appearance Rating <sup>(1)</sup>		Warp Shrinkage <sup>(1)</sup>	
				5L	20L	5L	20L
220	5	0.52	0.07	4.0	3.5	4.3%	4.1%
260	3	0.47	0.08	3.0	4.0	2.8	2.5
300	2	0.50	0.08	3.5	4.0	2.4	2.1
340	1	0.57	0.09	4.0	4.0	1.9	2.0
300	15	0.58	0.09	3.5	3.0	3.3	3.5
Control		—	0.04	—	—	8.3	—

<sup>(1)</sup> Determined on fabric laundered five and twenty times in an automatic washer with a rated capacity of 8 lbs. Fabric load was 8 lbs.; wash temperature was 105°F.; fabric was tumbled dried in an automatic clothes dryer. Rated on ATACC 5 (best) to 1 (poor) scale.

<sup>(2)</sup> Fabric scoured one hour at 200°F. in 0.25% chip soap and 0.50% soda ash, followed by thorough rinsing.

## EXAMPLE IV

In another set of samples using a mercerized and bleached 136 x 64 cotton broadcloth, an aqueous solution containing 2.5% formalde-

hyde, 1.0% methyl carbamate and catalyst as noted was applied at 60% wet pickup. The fabric was barely dried at 180°F (about 10% moisture) and heated at 260°F for 3 minutes.

5

TABLE 5

Sample	Catalyst System	% Formaldehyde <sup>(1)</sup> Fixed	% Nitrogen		Crease Angles Dry	Recovery (W+F) Wet
			Before Scour	After Scour		
1	{ 1% MgCl <sub>2</sub> ·6H <sub>2</sub> O 1% HCOOH	0.72	0.08	0.07	252°	212°
2	1% MgCl <sub>2</sub> ·6H <sub>2</sub> O	0.70	0.05	0.08	259°	246°
3	1% HCOOH	0.70	0.02	0.02	245°	234°
4	0.1% NH <sub>4</sub> Cl <sup>(2)</sup>	0.70	0.08	0.10	257°	242°
Control	—	—	0.02	0.04	127°	159°

(<sup>1</sup>) Fabric scoured one hour at 200°F. in 0.25% chip soap and 0.50% soda ash followed by thorough rinsing.

(<sup>2</sup>) Estimated. Bath was neutral — NH<sub>4</sub>Cl residual from preceding treatment of fabric.

- 10 Again only traces of nitrogen were found in the treated fabric, but it is important to note that the carbamate is not present on the fabric immediately after heating. This may be a clue in the determination of the mechanism of the reaction, because the carbamate is evidently decomposed by heating. A number of other samples have confirmed this observation.

## EXAMPLE V

Bleached, mercerized cotton yarn was treated in a kier with an aqueous solution containing 2.5% formaldehyde, 1.36% sodium chloride, 0.5% magnesium chloride hexahydrate, 0.5% formic acid, 0.1% dimethyl polysiloxane oil and the indicated amounts of methyl carbamate, and later dried at 180°F.

20

25

TABLE 6

Sample	Mole Ratio Formaldehyde to Methyl Carbamate	% Methyl Carbamate	% Formaldehyde Fixed
1	62.5:1	0.1	0.30
2	20.8:1	0.3	0.52
3	8.9:1	0.7	0.76
4	6.25:1	1.0	0.20
5	12.5:1	0.5	0.33



## EXAMPLE VI

A bleached, mercerized cotton yarn in a kier was treated with an aqueous solution containing 1.3% sodium chloride, 0.5% magnesium chloride hexahydrate, 0.5% formic acid, 0.1% dimethyl polysiloxane, 0.3% methyl carbamate and the indicated amounts of formaldehyde. The treated yarn was dried at 180°F.

TABLE 7

Sample	Mole Ratio Formaldehyde to Carbamate	% Formaldehyde in Solution	% Formaldehyde Fixed
1	2.5:1	0.3	0.05
2	7.5:1	0.9	0.24
3	12.5:1	1.5	0.40
4	17.5:1	2.1	0.34
5	22.5:1	2.7	0.52

## EXAMPLE VII

15 Mercerized cotton yarn was treated in a kier with an aqueous solution of the indicated amounts of materials and dried at 200°F. The methyl carbamate-formaldehyde precondensate was the condensation product of 2.5 moles

of formaldehyde with 1 of methyl carbamate and indicated in the table by MC-F. There was also present in the aqueous solution 0.5% of polyethylene softener and 0.1% an alkyl-phenol-ethylene oxide condensate as a wetting agent. 20

TABLE 8

Material	1	2	Sample 3	4
MC-F	4%	8%	4%	4%
MgCl <sub>2</sub> ·H <sub>2</sub> O	1%	1%	1.5%	—
Zn(BF <sub>4</sub> ) <sub>2</sub>	—	—	—	1%
H COOH	1%	1%	1.5%	1%
% CH <sub>2</sub> O fixed	0.63%	1.93%	1.02%	0.78%

No fixed nitrogen was observed in the yarn.

## EXAMPLE VIII

25 Both bleached, mercerized yarn and carded bleached cotton yarn were treated in a kier with an aqueous solution containing 2% of a methyl carbamate-formaldehyde precondensate (mole ratio 1:2.5), 2.1% free formaldehyde, 0.5% magnesium chloride, 0.5% formic acid, 2.5% sodium chloride, 0.2% sulfonated tallow (softener) and 0.025% of dimethyl polysiloxane. The yarns were dried at 200°F. 30 The mercerized yarn picked up 0.72% fixed formaldehyde and the carded yarn 0.70% fixed formaldehyde. 35

## EXAMPLE IX

40 Mercerized cotton yarn was treated in a kier with an aqueous solution of 0.5% ethyl carbamate, 2.1% formaldehyde (mole ratio formaldehyde to carbamate of 12.5:1), 0.5% magnesium chloride and 0.5% formic acid. The yarn was dried at 200°F to fix the formaldehyde to the yarn.

45 The ability of the carbamate-formaldehyde process of the present invention to reduce swelling of fabrics is shown in the following examples in the treatment of needle punched nonwoven rayon fabrics.

Thus, a fabric which consists of an 8 oz. viscose rayon nonwoven web (sold under the Trade Mark Avril) needled into a 1.6 oz. polypropylene scrim, calendered and palmered had an objectionable tendency to swell and increase in gauge during wet processing. This objection can be overcome in part by using a combination of polypropylene fiber and viscose rayon for the web. Because of the thermoplasticity of the polypropylene, this combination of fibers in the web can be hot calendered and palmered to reduce the gauge of the base fabric and to reduce swelling and gauge increase during predipping. However, this fabric still swelled and increased in gauge on wetting. Furthermore, the inclusion of the polypropylene fibers was a relatively expensive solution to the problem.

#### EXAMPLE X

The fabrics employed were as follows:

- (a) 8 oz. viscose rayon (Avril) web needle punched into a 1.6 oz. polypropylene scrim fabric,  
 (b) 8 oz. 60% polypropylene 40% 8 oz. viscose rayon (Avril) web needle punched into a 1.6 oz. polypropylene scrim fabric,  
 (c) 3.3 oz. 60% polypropylene 40% viscose rayon (Avril) web needled into a 1.0 oz. cotton scrim fabric.
- Fabrics (a), (b) and (c) were all needled, calendered and palmered.

The aqueous mixture applied to the fabrics contained:

methyl carbamate	1%	
formaldehyde	4%	35
magnesium chloride	0.83%	
formic acid	0.83%	
nonylphenol-ethylene oxide adduct (wetting agent)	0.2%	

This mixture is called Formulation A hereinafter.

Formulation A was applied at 120°F in a laboratory padder. Fabrics (a) and (b) were dried in a continuous oven at 250°F and fabric (c) was dried in the oven at 220°F, the fabrics were rolled up and held in a convection oven at 220°F for 1½ hours to simulate conditions obtained if the fabric should be wound up hot in commercial production. Thermocouples embedded in the fabric rolls indicated the temperature on the inside of the fabric roll to be

When placed in the oven	125°F	
After 25 minutes	170°F	
After 45 minutes	185°F	55
After 1 hour and 30 minutes	200°F	

The gauges of these fabrics, before and after treatment, were measured with a Starrett Model 1010 spring loaded hand micrometer with a ¼ inch anvil and ½ inch foot. The gauge was also measured after wetting in water.

	% Fixed Formaldehyde	Gauge (Dry)	Gauge (Saturated in Water)
Fabric (a) not treated	0	40 mils	68 mils
Fabric (a) treated	0.66%	45 "	59 "
Fabric (b) not treated	0	40 "	41 "
Fabric (b) treated	0.51%	34 "	36 "
Fabric (c) not treated	0	22 "	29 "
Fabric (c) treated	0.56%	23 "	25 "

- The treated sample in each pair had an appreciably lower wet gauge than did the fabric not treated. The treatment also caused further compression and restriction of fabric (b), a fabric which as constructed was devised to restrict swelling. The formaldehyde fixation in this and the following examples is based on the total weight of the fabric.

#### EXAMPLE XI

- The fabric employed was 8 oz. viscose rayon web needled into a 1.6 oz. polypropylene scrim, calendered and palmered.
- Formulation A (see Example X) was ap-

plied to one section of the fabric on a laboratory padder. One portion of this section was vacuum extracted between the top roll of the padder and the fabric wind-up. A second portion of this section was not vacuum extracted. Another section of the fabric was untreated. The fabrics were dried continuously in a laboratory oven at 250°F. A radiation pyrometer (Infrascopes) indicated the fabric temperature at the exit to be 221°F for the fabric vacuum extracted and 218°F on the fabric not vacuum extracted.

The results of swelling tests on these fabrics were as follows:

	% Fixed Formaldehyde	Gauge (dry)	Gauge Saturated With Water	Gauge Saturated 10% NaOH
Not Treated	0	39 mils	50 mils	70 mils
Treated	0.51%	48 "	47 "	—
Vacuum Extracted—Treated	0.68%	49 "	48 "	50 mils

5 The apparent slight decrease in gauge of the two treated fabrics is illusory since the results are the averages of ten readings and the variation is about  $\pm 2$  mils.

#### EXAMPLE XII

The fabrics employed were as follows:

10 (a) 8 oz. viscose rayon web needle punched into a 1.6 oz. polypropylene scrim fabric, calendered and palmered,

(b) 8 oz. 60% viscose rayon 40% polypropylene web needled into a 1.6 oz. polypropylene scrim,

15 (c) 8 oz. 60% viscose rayon 40% polypropylene web needled into a 1.6 oz. polypropylene scrim, calendered and palmered.

The treating solutions were:

Formulation A (See Example X)

20 Formulation B (the same as Formulation A, except it contained 8% of formaldehyde)

Formulation C (the same as Formulation A, except it contained 2% methyl carbamate and 8% formaldehyde).

25 The formulations were all applied at room temperature in a laboratory padder and vacuum extracted.

The fabrics were dried in a laboratory continuous dryer set at 260°F. The fabric treated

with Formulation A attained a surface temperature of 232°F, the fabric treated with 30 Formulation B attained a surface temperature of 214°F, and the fabric treated with Formulation C attained a surface temperature of 210°F. These differences in temperature had an influence on the level of formaldehyde 35 fixed in the fabric.

After drying, these fabrics were treated with sodium bisulfite solution to remove formaldehyde odor and recatalyzed with an aqueous mixture containing 0.83% each of  $MgCl_2$  and formic acid. The fabrics were then dried to the touch in a 300°F oven after the washing and recatalyzation. 40

The fabrics were hot calendered on a two-roll calender at 250°F and then palmered two passes at 260°F on one drum of a two-drum compressive shrinkage machine. 45

The swelling effect was determined as in Examples X and XI by gauging the fabric dry, saturated with water and saturated with 50 NaOH solution. Swelling characteristics were checked as finished in the laboratory (before calendering), after calendering and after calendering and palmering. The results of these tests and of formaldehyde analyses are 55 set forth in the following table:

Fabric	Formulation	% Fixed CH <sub>2</sub> O	Gauge (Dry)	Gauge	Gauge
				Saturated With Water	Saturated With 20% NaOH
(a)	Not treated	0	42 mils	54 mils	70 mils
(a)	A Before calendered	0.72	47	48	58
(a)	A Calendered	—	36	47	54
(a)	A Calendered and palmered	0.77	36	45	54
(a)	B Before Calendered	0.60	45	47	58
(a)	B Calendered	—	36	47	53
(a)	B Calendered and palmered	0.47	32	44	56
(a)	C Before Calendered	0.56	45	47	57
(a)	C Calendered	—	41	47	54
(a)	C Calendered and palmered	0.45	34	47	62
(b)	Not treated	0	62	58	68
(b)	A Before calendered	0.44	53	55	54
(b)	A Calendered	—	40	43	45
(b)	A Calendered and palmered	0.46	40	40	47
(c)	Not treated	0	28	32	42
(c)	A Before calendered	0.53	20	30	36
(c)	A Calendered	—	28	29	34
(c)	A Calendered and palmered	0.46	25	26	35

It is clear that the tendency of all of these fabrics in Example XII to swell in either water or in 20% NaOH has been reduced.

- 5 Fabric (b) not treated, Gauge (Dry) is an artificially high value because this particular fabric was in the fluffy condition. If it were in the normal compressed condition of the other fabrics, it would have had a gauge considerably below 58.

- 10 For significant reduction in the swelling of the fabrics, the fabrics usually contain a substantial amount of cellulose fibers, e.g. 10% or more, usually at least 20%.

- 15 Examples XIII and XIV demonstrate the speed at which processing of fabric is possible.

They also demonstrate the rapidity of the reaction which occurs under very favourable conditions.

#### EXAMPLE XIII

Three lightweight white fabrics containing blends of 65% polyester fiber and 35% cotton fiber were processed through an aqueous mixture containing 1.0% methyl carbamate, 6.0% formaldehyde, 0.83% magnesium chloride, 0.83% formic acid, 0.5% acrylic polymer, comprising ethyl acrylate, methyl methacrylate, acrylic acid and acrylamide (Rhoplex E-32), 0.25% polyvinyl alcohol and 0.2% nonyl phenol-ethylene oxide condensate (wetting agent) followed by drying.

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- The three fabrics included:
- a 125 x 72 3.70 yards/lb. (greige count and weight) broadcloth,
  - a 96 x 84 4.25 yards/lb. (greige count and weight) batiste,
  - a 94 x 80 4.34 yards/lb. (greige count and weight) batiste.

The polyester in fabrics (a) and (c) was Dacron, and in fabric (b) was Kodel. ("Dacron" and "Kodel" are Trade Marks).

The wet pick-up by these fabrics when passed through the mix on a padder was in the range of 35 to 40%.

Drying was accomplished on a tenter dryer with the air temperature regulated at 330°F. The speed of processing was 110 yards/min-

ute and the fabric dwell time in the dryer was 14 seconds.

Fabric temperatures obtained as indicated by an infrared pyrometer (Infrascopes) were in the range from 245 to 255°F.

After drying, the fabrics were padded through a sodium bisulfite solution to remove unreacted formaldehyde and obviate undesirable odors in the finished fabric (see Patent No. 890,515), washed and dried, a fatty acid based fabric softener was applied and dried into the fabrics, and the fabric was passed through a comprehensive shrinkage machine.

The fabrics were found to have fixed formaldehyde levels as indicated which remained essentially constant through multiple laundering.

#### % Formaldehyde Found<sup>(1)</sup>

Fabric Sample	As Finished (2)	After 5 Home Launderings <sup>(3)</sup>	After 5 Sanforize Washes <sup>(4)</sup>	After 5 Commercial White Washes <sup>(5)</sup>
a	0.62	0.56	0.50	0.53
b	0.59	0.56	0.56	0.52
c	0.62	0.61	0.62	0.61

<sup>(1)</sup> On total weight of the fabric.

<sup>(2)</sup> Scoured one hour at the boil in 1% soda ash.

<sup>(3)</sup> AATCC Tentative Test Method 88—1964T.

<sup>(4)</sup> One hour wash procedure. Starts near the boil.

<sup>(5)</sup> 160°F wash, chlorine bleach, zinc silicofluoride sour 37 minute cycle. ("Sanforize" is a Trade Mark.)

- In addition, these fabrics had excellent wash-wear properties, retained a crisp hand through multiple laundering, remained white in multiple launderings while fabric not treated lost whiteness. In a commercial laundering with coloured garments, the untreated fabric stained badly, while the treated fabric stained only slightly under such conditions.

#### EXAMPLE XIV

- The three fabrics of Example XIII were passed through a mixture containing 1.0% methyl carbamate, 4.0% formaldehyde, 0.83% magnesium chloride, 0.83% formic acid, 0.5% acrylic polymer (Rhoplex E-32), 0.7% fatty acid based softener and 0.2% nonyl phenol-ethylene oxide condensate (wetting agent).

- These fabrics were dried under similar conditions to those in Example XIII, except that the speed was 90 yards/minute and the fabric temperature as indicated by an infrared pyrometer was in the range from 250—260°F.

These fabrics were processed after treatment as in Example XIII with bisulfite and softener, except that the mixture including the softener also included 1.4%  $MgCl_2$  and 1.4%  $HCOOH$ .

These fabrics were just barely dried after application of the mixture containing  $MgCl_2$  and  $HCOOH$  to prevent excessive loss of the acid.

These fabrics had the properties of the fabrics of Example XIII and also had the ability to retain a sharp crease after pressing and laundering. Thus, swatches of the fabrics were creased by pressing 15 seconds at a steam pressure of 100 psig in a Forse laundry press. The creases remained sharp and smooth throughout multiple laundering. This example throughout multiple laundering.

This example demonstrates that the present invention can be utilized to impart durable shape retention and durable press to treated fabrics.

## EXAMPLE XV

A heavy (8.6 oz./sq. yard) all cotton twill fabric which was previously mercerized and dyed was passed through an aqueous mixture containing:

- 5 1.0% methyl carbamate  
4.0% formaldehyde  
0.83%  $\text{MgCl}_2$   
0.83%  $\text{HCOOH}$   
10 1.0% acrylic polymer (Rhoplex E-32)  
0.5% polyvinyl alcohol  
0.2% nonyl phenol-ethylene oxide condensate (wetting agent)

15 The fabric was dried in a tenter dryer set at air temperature of 330°F. The fabric temperature was 230°F as measured by an infrared pyrometer. Dwell time in the oven was 21 seconds.

20 The fabric was then passed through an aqueous buffered catalyst mixture containing:

- 25 0.83%  $\text{MgCl}_2$   
0.83%  $\text{HCOOH}$   
0.50%  $\text{Na}_2\text{S}_2\text{O}_5$  (sodium meta bisulfite)  
2.5% emulsified tallow softener

The fabric was dried in a tenter dryer set at an air temperature of 250°F. The fabric temperature was 190°F.

30 Swatches of the fabric were creased by pressing in a steam heated laundry press for 15 seconds at 100 psig steam followed by heating in a convection oven set at 325°F. for six minutes.

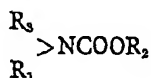
35 When these fabrics were given multiple washings, the creases were retained and appearance of the fabrics was excellent.

Similar results were obtained when the pressed fabrics were placed in a convection oven at 275°F for six minutes.

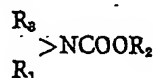
40 As indicated in Example XV, for crease retention it is desirable to add further catalyst to compensate for the catalyst lost in the initial heating employed to dry the formaldehyde treated fabric. The crease retention properties are then imparted after the  
45 initial cure of the fabric.

## WHAT WE CLAIM IS:—

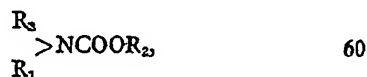
1. A process of fixing an aldehyde on cellulose, a cellulose ester, or starch, comprising the steps of treating the material with an aqueous composition containing (1) an aldehyde and a carbamate having the formula



55 (2) an aldehyde-carbamate condensation product wherein the carbamate has the formula



or (3) an aldehyde together with an aldehyde-carbamate condensation product wherein the carbamate has the formula



wherein  $\text{R}_1$  and  $\text{R}_3$  are each hydrogen or alkyl or carbocyclic aryl radicals at least one of  $\text{R}_1$  and  $\text{R}_3$  representing a hydrogen atom in the case of an aldehyde-carbamate condensation product, and  $\text{R}_2$  is an unsubstituted alkyl or a cycloalkyl or carbocyclic aryl radical, and heating the treated material at a temperature sufficient to fix the aldehyde on the material but insufficient to cause any substantial nitrogen fixation.

2. A process as claimed in claim 1 in which  $\text{R}_1$  and  $\text{R}_3$  each represent hydrogen.

3. A process as claimed in claim 1 or 2 in which the aldehyde is formaldehyde.

4. A process as claimed in claim 1, 2 or 3 in which the aqueous composition includes an acidic catalyst.

5. A process as claimed in claim 1, 2 or 3 in which the aqueous composition includes a latent acidic catalyst.

6. A process as claimed in claim 1, 2 or 3 in which the aqueous composition includes a basic catalyst.

7. A process as claimed in any of claims 1 to 6 in which  $\text{R}_2$  is an unsubstituted lower alkyl radical.

8. A process as claimed in any one of claims 1 to 7 in which the carbamate is an alkyl carbamate which is used in an amount of at least 0.1% up to 5% by weight of the aqueous composition.

9. A process as claimed in claim 8 in which the alkyl carbamate is used in an amount of at least 0.3% up to 1% by weight of the aqueous composition.

10. A process as claimed in claim 9 in which the alkyl carbamate is used in an amount of at least 0.5% up to 1% by weight of the aqueous composition.

11. A process as claimed in any of claims 1 to 10 in which the aldehyde is used in an amount of from 3 to 60 moles per mole of carbamate.

12. A process as claimed in any of claims 1 to 11 in which the carbamate is methyl or ethyl carbamate.

13. A process as claimed in any of claims 1 to 12 in which the heating is at a temperature of 180°F to 300°F.

14. A process as claimed in any of claims 1 to 13 in which the aldehyde is fixed on cotton.

15. A process as claimed in any of claims 1 to 13 in which the aldehyde is fixed on regenerated cellulose.
- 5 16. A process as claimed in any of claims 1 to 13 in which the aldehyde is formaldehyde which is fixed on cellulose in an amount from 0.25% to 1.25% based on the weight of the cellulose, and the cellulose is in the form of cotton.
- 10 17. A process as claimed in any of claims 1 to 13 in which the aldehyde is formaldehyde which is fixed on cellulose in an amount from 0.5% to 2.5% based on the weight of the cellulose, and the cellulose is in the form of regenerated cellulose.
- 15 18. A process as claimed in any of claims 1 to 17 in which the fibres comprise a substantial percentage of regenerated cellulose fibres.
- 20 19. A process as claimed in any of claims 1 to 17 in which the fibres comprise at least 35% by weight viscose rayon fibres.
- 25 20. A process as claimed in any of claims 1 to 17 in which the aldehyde is fixed on a fabric comprising fibres of cellulose and/or a cellulose ester.
- 30 21. A process as claimed in claim 20 including the further step of adding additional catalyst to the treated fabric, drying the further catalyzed fabric and pressing and heating the fabric to obtain a shape and crease retentive fabric.
- 35 22. A process as claimed in claim 21 in which said catalysts are acidic catalysts.
- 40 23. A process as claimed in any of claims 1 to 22 in which the aldehyde is liberated in situ from a substance yielding an aldehyde.
- 45 24. A process of fixing an aldehyde on cellulose, a cellulose ester or starch substantially as herein described with reference to and illustrated in any of Examples I to IX.
- 50 25. A process of fixing an aldehyde on cellulose, a cellulose ester or starch substantially as herein described with reference to and illustrated in any of Examples X to XV.
- 55 26. A product prepared by a process as claimed in any of claims 1 to 25.
27. A product prepared by treating cellulose, a cellulose ester, or starch with an aqueous mixture of formaldehyde and an alkyl carbamate, and heating the treated material to fix the formaldehyde thereon.
28. A product as claimed in claim 27 in which the cellulose is regenerated cellulose.
29. A product as claimed in claim 28 in which the regenerated cellulose is viscose rayon.
30. A product as claimed in claim 27 in which the cellulose is cotton.
31. A process of fixing an aldehyde on cellulose, a cellulose ester or starch, comprising the steps of treating the material with an aqueous composition containing (1) an aldehyde and an unsubstituted alkyl carbamate, (2) an aldehyde-unsubstituted alkyl carbamate condensation product, or (3) an aldehyde together with an aldehyde-unsubstituted alkyl carbamate condensation product, and heating said treated material at a temperature sufficient to fix the aldehyde on said material but insufficient to cause any substantial nitrogen fixation on the polymer.
32. A process as claimed in claim 31 in which the aldehyde is formaldehyde.
33. A process as claimed in claim 31 or 32 in which the alkyl carbamate is a lower alkyl carbamate.
34. A process as claimed in claim 31, 32 or 33 in which the alkyl carbamate is used in an amount of at least 0.1% up to 5% of the aqueous composition.
35. A process as claimed in any of claims 31 to 34 in which the aldehyde is used in an amount of from 3 to 60 moles per mole of carbamate.
36. A process as claimed in any of claims 31 to 35 in which carbamate is methyl or ethyl carbamate.
37. A process as claimed in any of claims 31 to 36 in which the heating is at a temperature of 180°F. to 300°F.
38. A process as claimed in any of claims 31 to 37 in which the aldehyde is fixed on cotton.
39. A process as claimed in any of claims 31 to 37 in which the aldehyde is fixed on regenerated cellulose.
40. A process as claimed in any of claims 31 to 37 in which the aldehyde is formaldehyde which is fixed on cellulose in an amount from 0.25% to 1.25% based on the weight of the cellulose, and the cellulose is in the form of cotton.
41. A process as claimed in any of claims 31 to 37 in which the aldehyde is formaldehyde which is fixed on cellulose in an amount from 0.5% to 2.5% based on the weight of the cellulose, and the cellulose is in the form of regenerated cellulose.

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